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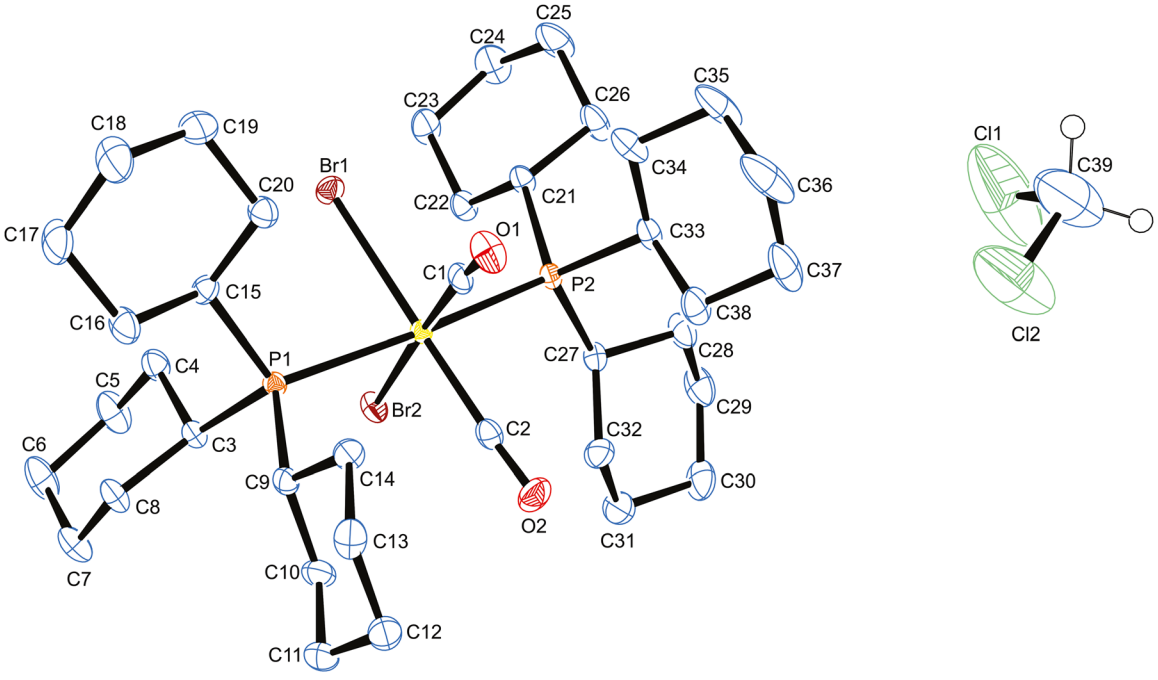
Crystal structure of dibromo-dicarbonyl-bis(tricyclohexylphosphine)-osmium(II) dichloromethane solvate, $C_{38}H_{66}Br_2O_2OsP_2$



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Abstract

$C_{38}H_{66}Br_2O_2OsP_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.4091(2) Å, b = 10.6868(2) Å, c = 21.3533(4) Å, α = 84.658(1)°, β = 89.764(1)°, γ = 64.918(1)°, V = 2140.36(7) Å^3, Z = 2, $R_{gt}(F)$ = 0.0248, w$R_{ref}(F^2)$ = 0.0578, T = 173(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.67 × 0.42 × 0.21 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	5.08 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon, ω
θ_{max}, completeness:	28.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	86,068, 10,330, 0.045
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 9863
$N(param)_{refined}$:	433
Programs:	Bruker [1], WinGX/ORTEP [2], SHELX [3], PLATON [4]

1 Source of materials

All reagents are commercially available and were used without further purification. The $(NH_4)_2[OsBr_6]$ (2.04 g, 2.89 mmol) and 2-ethoxyethanol (70 mL) were loaded into an autoclave which was then pressurised with 10^3 kPa carbon monoxide gas. The reaction mixture was heated to 140 °C with stirring for 48 h. To the filtered reaction mixture was added tricyclohexylphosphine (3.39 g, 12.1 mmol) and the solution

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3073 (3)	0.1319 (3)	0.28233 (13)	0.0196 (6)
C2	0.2371 (3)	0.3738 (3)	0.22585 (13)	0.0188 (6)
C3	0.1641 (3)	0.1899 (3)	0.06258 (13)	0.0158 (5)
H3	0.11704	0.293547	0.060657	0.019*
C4	0.0419 (3)	0.1453 (3)	0.06191 (14)	0.0220 (6)
H4A	0.080441	0.04437	0.058065	0.026*
H4B	−0.007931	0.163589	0.101974	0.026*
C5	−0.0630 (3)	0.2252 (4)	0.00674 (15)	0.0313 (8)
H5A	−0.137942	0.191451	0.005647	0.038*
H5B	−0.109013	0.324956	0.013343	0.038*
C6	0.0092 (4)	0.2087 (4)	−0.05652 (16)	0.0344 (8)
H6A	0.040088	0.112015	−0.066934	0.041*
H6B	−0.059811	0.271217	−0.089946	0.041*
C7	0.1366 (4)	0.2424 (4)	−0.05471 (15)	0.0296 (7)
H7A	0.103938	0.342664	−0.050468	0.036*
H7B	0.186021	0.222471	−0.09479	0.036*
C8	0.2404 (3)	0.1578 (3)	0.00016 (13)	0.0224 (6)
H8A	0.322478	0.181721	0.000161	0.027*
H8B	0.276196	0.057438	−0.004554	0.027*
C9	0.4329 (3)	0.1596 (3)	0.11453 (13)	0.0167 (5)
H9	0.475104	0.100774	0.07945	0.02*
C10	0.3986 (3)	0.3091 (3)	0.08819 (15)	0.0226 (6)
H10A	0.354704	0.37231	0.121006	0.027*
H10B	0.329577	0.336895	0.052093	0.027*
C11	0.5334 (4)	0.3225 (4)	0.06676 (15)	0.0260 (7)
H11A	0.570701	0.267864	0.030503	0.031*
H11B	0.509621	0.420933	0.052674	0.031*
C12	0.6470 (4)	0.2715 (4)	0.11918 (16)	0.0269 (7)
H12A	0.613537	0.332036	0.153741	0.032*
H12B	0.733827	0.277323	0.10307	0.032*
C13	0.6821 (3)	0.1224 (3)	0.14452 (16)	0.0242 (6)
H13A	0.753411	0.093101	0.179811	0.029*
H13B	0.723611	0.060489	0.110983	0.029*
C14	0.5487 (3)	0.1088 (3)	0.16739 (14)	0.0191 (6)
H14A	0.512211	0.164101	0.203495	0.023*
H14B	0.572879	0.010424	0.181929	0.023*
C15	0.3373 (3)	−0.0614 (3)	0.14722 (13)	0.0168 (5)
H15	0.252137	−0.078065	0.13773	0.02*
C16	0.4488 (4)	−0.1397 (3)	0.10039 (15)	0.0250 (6)
H16A	0.415258	−0.095879	0.057077	0.03*
H16B	0.53873	−0.133169	0.109688	0.03*
C17	0.4757 (5)	−0.2927 (4)	0.10453 (17)	0.0365 (9)
H17A	0.387738	−0.299434	0.091709	0.044*
H17B	0.550171	−0.341368	0.075151	0.044*
C18	0.5224 (5)	−0.3627 (4)	0.17112 (18)	0.0430 (10)
H18A	0.616049	−0.365763	0.182106	0.052*
H18B	0.53251	−0.459361	0.173192	0.052*
C19	0.4151 (4)	−0.2847 (3)	0.21833 (17)	0.0327 (8)
H19A	0.450325	−0.329069	0.26143	0.039*
H19B	0.324089	−0.289803	0.209994	0.039*
C20	0.3908 (3)	−0.1331 (3)	0.21395 (14)	0.0206 (6)
H20A	0.480785	−0.127851	0.224577	0.025*
H20B	0.320195	−0.084293	0.244746	0.025*
C21	−0.1342 (3)	0.3090 (3)	0.33765 (13)	0.0173 (5)
H21	−0.086355	0.205798	0.337352	0.021*
C22	−0.2551 (3)	0.3592 (3)	0.28709 (14)	0.0205 (6)
H22A	−0.316165	0.459286	0.288936	0.025*
H22B	−0.21489	0.346833	0.244811	0.025*
C23	−0.3434 (4)	0.2769 (4)	0.29799 (16)	0.0279 (7)
H23A	−0.284046	0.178549	0.291667	0.034*
H23B	−0.423652	0.313323	0.266565	0.034*
C24	−0.4012 (4)	0.2848 (5)	0.36383 (17)	0.0350 (8)
H24A	−0.473543	0.380326	0.367716	0.042*
H24B	−0.447996	0.221207	0.37038	0.042*
C25	−0.2842 (4)	0.2456 (5)	0.41429 (16)	0.0374 (9)
H25A	−0.218978	0.146075	0.414411	0.045*
H25B	−0.326605	0.260012	0.456102	0.045*
C26	−0.2006 (4)	0.3334 (4)	0.40251 (15)	0.0292 (7)
H26A	−0.125037	0.306743	0.435752	0.035*
H26B	−0.264628	0.43295	0.403596	0.035*
C27	−0.0948 (3)	0.5617 (3)	0.29945 (13)	0.0178 (5)
H27	−0.178864	0.575584	0.272417	0.021*
C28	−0.1579 (4)	0.6381 (3)	0.35785 (15)	0.0273 (7)
H28A	−0.205625	0.588658	0.38288	0.033*
H28B	−0.080677	0.638591	0.384615	0.033*
C29	−0.2646 (4)	0.7874 (4)	0.33779 (16)	0.0321 (8)
H29A	−0.345419	0.786282	0.313923	0.039*
H29B	−0.301987	0.835716	0.375751	0.039*
C30	−0.1979 (4)	0.8667 (4)	0.29724 (17)	0.0328 (8)
H30A	−0.126492	0.879811	0.322954	0.039*
H30B	−0.272058	0.959587	0.281952	0.039*
C31	−0.1270 (4)	0.7895 (3)	0.24119 (16)	0.0297 (7)
H31A	−0.076891	0.839143	0.218109	0.036*
H31B	−0.200734	0.789085	0.212175	0.036*
C32	−0.0209 (3)	0.6394 (3)	0.26133 (15)	0.0235 (6)
H32A	0.019569	0.591607	0.223573	0.028*
H32B	0.057912	0.639273	0.287199	0.028*
C33	0.1015 (3)	0.3402 (3)	0.39277 (13)	0.0196 (6)
H33	0.029962	0.396531	0.422269	0.024*
C34	0.1606 (4)	0.1888 (4)	0.42206 (15)	0.0272 (7)
H34A	0.082933	0.158534	0.425142	0.033*
H34B	0.232749	0.128466	0.394568	0.033*
C35	0.2278 (4)	0.1729 (5)	0.48754 (16)	0.0414 (10)
H35A	0.153678	0.225723	0.516214	0.05*
H35B	0.269732	0.073824	0.504459	0.05*
C36	0.3428 (4)	0.2260 (6)	0.48490 (18)	0.0533 (13)
H36A	0.381572	0.218943	0.528007	0.064*
H36B	0.421311	0.167105	0.459558	0.064*
C37	0.2851 (4)	0.3747 (5)	0.45633 (17)	0.0438 (11)
H37A	0.362971	0.404735	0.453699	0.053*
H37B	0.212905	0.434715	0.483896	0.053*
C38	0.2179 (3)	0.3929 (4)	0.39040 (15)	0.0263 (7)
H38A	0.291804	0.340447	0.361562	0.032*
H38B	0.176466	0.492274	0.373979	0.032*
O1	0.4062 (2)	0.0673 (2)	0.31308 (11)	0.0275 (5)
O2	0.2958 (3)	0.4430 (3)	0.22720 (12)	0.0288 (5)
P1	0.27457 (7)	0.13132 (7)	0.13718 (3)	0.01277 (13)
P2	0.00499 (7)	0.36961 (8)	0.31623 (3)	0.01408 (13)
Br1	0.03599 (3)	0.07790 (3)	0.23555 (2)	0.01901 (6)
Br2	−0.05509 (3)	0.42259 (3)	0.15482 (2)	0.01927 (6)
Os1	0.15202 (2)	0.25086 (2)	0.22915 (2)	0.01191 (3)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C39	0.7773 (6)	0.1993 (8)	0.6295 (3)	0.0794 (19)
H39A	0.800665	0.112789	0.657573	0.095*
H39B	0.781932	0.269389	0.655582	0.095*
Cl1	0.6102 (2)	0.2562 (3)	0.60053 (8)	0.1335 (10)
Cl2	0.90602 (17)	0.1667 (2)	0.57297 (7)	0.0971 (7)

was then heated to reflux for a further 3 h in a Schlenk tube under Ar. After cooling to room temperature a white precipitate was obtained which was isolated by filtration. The product was washed with hexane and dried *in vacuo*. The title compound was obtained as a white solid. Yield (2.57 g, 92 %). Crystals of the compound were obtained by slow evaporation, at ambient temperature, of a dichloromethane solution over several days. The title compound was obtained as a solvate with a molecule of dichloromethane.

2 Experimental details

Intensity data were determined on a Bruker D8 Venture with Photon III CCD area detector diffractometer at 173 K using an Oxford Cryostream 600 cooler. Data reduction was carried out using the program SAINT+, version 6.02 [1] and empirical absorption corrections were made using SADABS [1]. The structure was solved in the WinGX [2] suite of programs, using intrinsic phasing through SHELXT [3] and refined using full-matrix least-squares/difference Fourier techniques on F^2 using SHELXL-2018/3 [3]. All C-bound hydrogen atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times or 1.5 times those of their parent atoms. Diagrams and publication material were generated using ORTEP-3 [2], and PLATON [4].

3 Comment

The chemistry of osmium is of interest due to the potential of these complexes in the future development of therapeutic and diagnostic agents in cancer and other areas of medicine [5–8]. The bioorganometallic properties of these complexes are directed by ligand effects, geometry, kinetic and thermodynamic properties of the complex as well as the oxidation state of the metal. The coordination architecture of these metal complexes provides a framework for structural diversity which allows for the design of new anticancer agents with novel mechanisms of action. The title compound is of interest because it contains labile bromide ligands as well as lipophilic tricyclohexylphosphine ligands. The *cis*-configuration of the labile halide ligands has been shown to be a key structural feature for anticancer activity [9].

The crystal structure of the title compound is isostructural with the *cis,cis,trans*-$[OsF_2(CO)_2\{P(C_6H_{11})_3\}_2]$ complex previously reported by Coleman *et al.* [10]. The osmium(II) metal ion is coordinated by two mutually *trans*, bulky tricyclohexylphosphine ligands in the axial positions to minimise steric interactions. The two bromide ligands and two carbonyl ligands are located in the equatorial plane in mutually *cis* positions. The Os—C=O moieties are distorted slightly from linearity with bond angles of 174.29° and 175.11° as a result of π back-bonding from osmium. All geometric parameters are in the expected ranges [11].

In the crystal, there is evidence of intramolecular interactions between hydrogen atoms of the PCy_3 ligands and the bromide ligands. Nonbonding intramolecular interactions are observed between Br(1)···H(4B) at 2.890 Å, Br(1)···H(20B) at 2.718 Å, Br(2)···H(22B) at 2.818 and Br(2)···H(32A) at 2.778 Å. In addition, there is an intermolecular interaction observed between Br(1)···H(39A) at 2.912 Å. These noncovalent interactions contribute to the orientation of the tricyclohexylphosphine ligand and the packing arrangement in the crystal.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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